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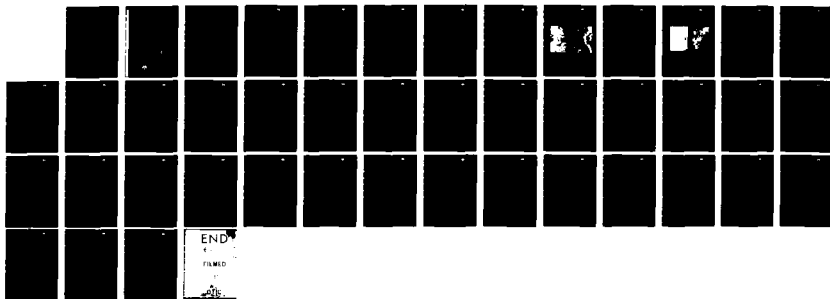
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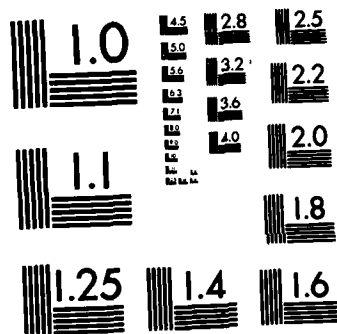
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**SYNTHETIC STUDIES OF ANTIMONY SULFUR IODIDE
AND PREDICTION/SYNTHESIS OF NEW NITROGEN
CONTAINING CRYSTAL STRUCTURES**

**FINAL REPORT FOR THE PERIOD
September 1, 1979 through December 1, 1981**

CONTRACT NO. N00014-79-C-0709

Prepared for

**Material Sciences Division
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217**

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Principal Investigator**

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ABSTRACT

SbSI has been grown to needles ~ 1 mm long by hydrothermal techniques. The curious bonding in this compound is discussed. The possible use of Pauling's Second Crystal Rule for predicting anion aliovalent substitution in crystallographic isotypes, particularly of nitrogen, is examined. Bond length/bond strength sums are also reviewed for structures where N-substitution is known. It is predicted that many nitrogen-phosphate mineral type structures can be made.



PART I. STUDIES OF THE PREPARATION OF ACICULAR SbSI

INTRODUCTION

The interesting ferroelectric properties of antimony sulfur iodide (SbSI) are well-documented in the literature.¹ Following the work of Okazaki,² it appeared likely that well-aligned SbSI would have extremely useful piezoelectric properties. It was appreciated that a source of high purity powder was necessary to prepare good SbSI polycrystalline ceramics for potential hydrophone use. The author was asked to investigate the production of pure SbSI and supply a quantity of powder for testing at the Naval Research Lab. It was noticed at this time that the powder was acicular (not unexpected), and it was immediately realized that just as acicular magnetic powders can be aligned in a magnetic field, so also could some ferroelectric materials be aligned in an electric field, and this was immediately tested.^{3,4}

It was proposed to study the formation of better powders with larger acicular needles.³ Meanwhile, an apparatus was constructed at Naval Research Labs and the concept tested,⁵ not only on the powder supplied by the author, but also upon a Gallard-Schlesinger powder (quite impure and giving a yellow decomposition product upon standing in air). Furthermore, at NRL a sample of needles produced by breaking up "single crystal" boules showed extremely interesting properties and an apparent improvement was the adaptation of the original direct field method to an alternating (60 Hz) concept.⁵

It was clear, therefore, that further developments in preparing larger acicular powder specimens would be useful. Moreover, the testing of the field alignment technique would be a prototype situation for preparing other ferroelectric materials in a highly anisotropic form.

The basic method of first forming SbSI powders is that of Francois:⁶ solutions, containing Sb^{3+} and HI at the level of 25 w/o, precipitate SbSI when treated with H_2S gas.



EXPERIMENTAL AND RESULTS

SbSI crystals can be grown hydrothermally,^{7,8} but we attempted a simplification. As a first attempt, a bent glass tube apparatus was constructed in such a way that one glass arm was immersed in oil at $\sim 120^{\circ}\text{C}$. In this arm was placed finely powdered SbSI and in a saturated solution of Sb^{3+} in 25 w/o HI and H_2S ; the other end of the apparatus was air- or water-cooled. A loose glass wool plug was inserted between the hot and cool ends to prevent floating crystals passing from one end to the other. The glass tube was sealed with a screw-on clamp to be able to withstand the pressure (several atmospheres) on heating and avoid evolution of HI or H_2S .

The first small version of the apparatus, ~ 10 cm long, worked quite well. The powder dissolved at the hot end and large "sea urchin" crystals grew over a period of several days at the cooler end. These are shown in Fig. 1. When a much larger apparatus was made with a tube about 25 cm long and 4 cm diameter, it was found difficult to get good crystals, even after about six tries.

The method was abandoned in favor of another design. A tube 6 cm in diameter and 15 cm long was filled with the Sb/HI/ H_2S liquid. A bag was made of glass fabric (typical drapery material) and filled with fine SbSI powder. The bag was suspended at the top of a sealed tube, which was heated with heating tape to $\sim 120^{\circ}\text{C}$. The lower end of the tube remained cool and was not insulated. The powder dissolved in the hot liquid and coarse crystals grew at the bottom (cold) end. This was an adaptation of the normal crystal growing concept where transport down the tube is by diffusion only; convection is avoided by having the top hotter than the bottom. Many batches (about 20 g each) were successful, except that we could not avoid contamination with a few glass fibers. Careful removal of loose ends and double bags did not solve the problem.

It was clear in the earlier work that 120°C was sufficient to recrystallize SbSI over a period of several days. It was decided, therefore, to



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(a)



(b)

Fig. 1 SbSI needles, 120°C, 25 w/o HI, 3 days.



try the recrystallization in teflon lined stainless steel hydrothermal bombs at 150°C (the maximum temperature for this type of bomb).

The starting powder was tightly packed into the teflon inner containers* to the top (4 cm diameter by 5 cm long), and just enough $\text{Sb}^{3+} + \text{HI} + \text{H}_2\text{S}$ liquid (left over from the precipitation) to cover the powder completely wetting it. The seal was made by the teflon lid when screwed down. After 3 or 4 days in a 150° oven, the material was removed and seen to have grown by about 10X (Fig. 2). Especially at the top of the sample, a few, much larger deep wine red crystals had grown. XRD confirmed that the product was pure SbSI with normal lattice parameters.⁹ After one day of recrystallization, the crystals were smaller than for 3 or 4 days, so the latter was settled on as a practical limit. Longer times seemed not to greatly affect the crystal size and the chance of leakage increased. The initial agglomerates of needles had disappeared and the new crystals were more loosely packed and appeared to be not bonded together strongly (Fig. 2). These pictures reproduce somewhat poorly from red-color original light micrographs. It is suggested that these needles will be more easily field-aligned, and a couple of batches have been provided to Roy Rice, NRL, for this purpose.

In conclusion, then, needles of < 1 mm are quite easily grown at 150°C in the $\text{HI}/\text{H}_2\text{S}$ liquid, but for longer needles, higher temperatures, e.g., 250-300°C^{7,8} would be required.

It has been of continuing interest to attempt to raise the Curie temperature of the material. It was suggested earlier that the incorporation of oxygen into the material raised T_c . However, this has not been confirmed. It is the opinion of the author that to produce crystals with oxygen content would be difficult in a hydrothermal environment. It might be easier to introduce oxygen, if possible, in the fabrication step. The earlier

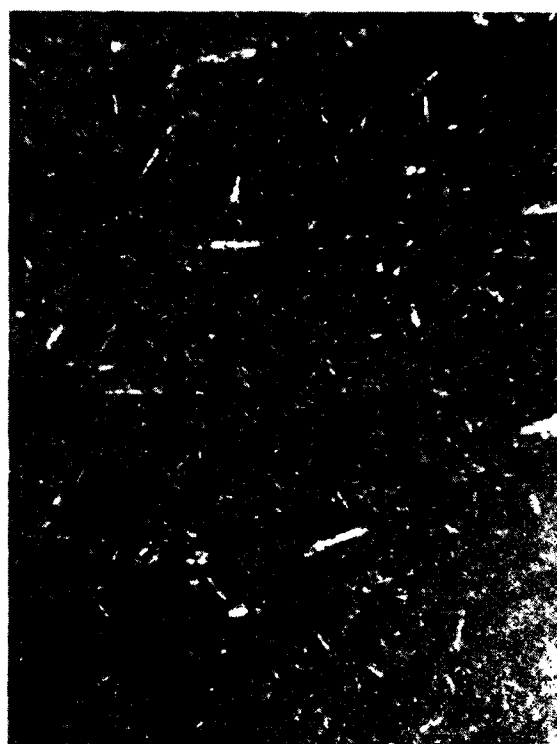
*"Universal Decomposition Vessels" manufactured by Columbia Organic Chemicals, Columbia, S.C.



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(a)



(b)

Fig. 2 Growth of SbSI needles. (a) As precipitates. (b) Hydrothermal in Teflon "bombs" at 120°C 25 w/o HI, 3 days.



supposition may have been related to effects that are seen when fine particles are separated from each other, possibly by thin films of other materials, e.g., Sb_2S_3 ¹⁰ and for hot-pressed material.⁵

Another approach, apparently not yet tested out on macro-body, is that it appears that T_c is raised by putting the long needle, c, axis of SbSI in tension.¹¹ With sufficiently oriented strong hot-pressed bodies, this might be possible. Ultimately, by the Poisson effect, the same end might be achieved by a biaxial compression in the a,b axes directions. This should be tested on highly aligned bodies.

The bonding in SbSI is extremely unusual;^{9,12} a chemist perforce relates the physical properties to perceptions of bonding. Thus, the mechanical properties of this substance are dominated by the stronger bonds running approximately in the c-axis direction of the orthorhombic unit cell and the much weaker interactions approximately perpendicular to this axis. This has led to a description of the material as a "pantograph."¹²

The unusual ferroelectric related properties, i.e., optical and acoustic properties¹ in this case can clearly be associated with the relative atomic and electronic displacements (although the measurements are, of course, not complete), in such a way that some predictions could emerge for future enhanced physical properties.

What is immediately clear is that the likelihood of this behavior is increased for elements at the high end of the periodic table where bonding is more irregular, with lone pair and empty orbital effects increasing. Both Sb and I are known to exhibit unusual bonding coordinations with "secondary" bonds quite common.¹³ That SbSI has this very unusual bonding relationship is not surprising. We would note immediately that for pantographic action we need large, easily polarizable atoms, where angular relations are easier to change when large atoms have less strict coordination relationships. Indeed, although the other members of the family containing As, Bi, Te, Br, etc., have the same structure, the detailed bonding and secondary bonding are obviously significantly different in line with the much lower Curie temperatures of these crystals.



In order to examine the bonding in SbSI (even in this simple way) we must relate the bond lengths to approximately normal Van der Waals and single bond distances; Table 1 gives these values¹³ with the bond lengths found from the refinement⁹ for nearest neighbors. A large number of long, or secondary bonds, are evident. In fact, only one or two bonds are near normal single bonds. This, as mentioned, is a particular characteristic of Sb-S and Sb-I chemistry. For example SbI₃ frequently shows secondary links where e.g., AsBr₃, SbCl₃ and SbBr₃ and BiI₃ do not.¹⁴ The compound SbI₃.S₂C₄H₄ similarly has a long Sb-S bond.¹⁵ Unfortunately, we do not yet have bond strength/bond length values for these bonds (for example the Brown, Shannon, Wu type values, of which more later) to assess the strengths. Nonetheless, the physical properties are undoubtedly related to these long bonds and the importance of SbSI and related compounds should stimulate more work on this. New techniques are just emerging which will allow better electron density mapping for heavy elements^{16a} and this will be extremely helpful. However, the relation of bonding to electron density is still obscure and the usefulness of e.g., MO calculations to a materials scientist in these structures is still very limited.



Table 1
Van der Waals, Single Bond (SB) Distances and SBSI Bond Lengths Compared^{9,13}

	Van der Waals	Sb	Paraelectric SbSI	Ferroelectric SbSI
Sb-Sb	4.10	2.72	3.8267(x2)*	3.8228(x2)*
Sb-I	4.03	2.64	3.8130(x2),* 3.0982(x2) [‡]	3.9263,* 3.7139,* 3.2471,* 2.9868 [‡]
I-I	3.96	2.56	---	---
Sb-S	3.85	2.40	3.8057,* 2.7232(x2) [‡] 2.4920	3.8259,* 2.8339, [‡] 2.6058, 2.4748
I-S	3.78	2.32	3.7125(x2)*	3.7421,* 3.6907*
S-S	3.60	2.08	3.5508(x2)*	3.5165(x2)*

Coordinations of nearest neighbors:

Sb; 2 bonds → Sb, 4 bonds → I, 4 bonds → S
I; 4 bonds → Sb, 2 bonds → S
S; 4 bonds → Sb, 2 bonds → I, 2 bonds → S

Structure characterized by:

* Weak and long bonds.
‡ Intermediate strength bonds
Only one or two strong bonds
cf SbI₃, Sb-I bonds, 3.32(x3),
2.868(x3)
SbI₃·S₂C₄H₄, Sb-I, 2.77(x3),
Sb-S, 3.27
Sb(S₂COC₂H₅)₃, Sb-S, 2.52,
3.00



PART II. THE USE OF BOND SUMS TO ATTEMPT THE PREDICTION
OF ISOMORPHOUS N-SUBSTITUTED CRYSTAL STRUCTURES

INTRODUCTION

Pauling's second crystal rule (PSCR), in its modern form, states that the bond strength sum from cations arriving at an anion nearly equals the valence of the anion. The bond strength arriving from each cation is approximately the valence (not in the modern form, charge) of the cation divided by its coordination. This assumes that all bonds on a cation are of equal strength. Thus:

$$V_{\text{anion}} \approx \sum_1^N \frac{V_{\text{cation}}}{C_{\text{cation}}}$$

This rule was found to work remarkably well with the early crystal structures that were examined by x-ray diffraction (XRD), which were mostly oxide mineral types, and it greatly simplified the guessing of trial structures. It does not work well for many sulfides. Garnet would exemplify this rule; in garnet, prototypically $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, grossular, we have Ca^{VIII} , Al^{VI} , Si^{IV} and O^{IV} (roman numerals denote coordination, arabic numbers will be valence). Each oxygen is coordinated to $2\text{Ca} + 1\text{Al} + 1\text{Si}$ so that the bond sum at oxygen is $\frac{2 \times 2}{8} + \frac{1 \times 3}{6} + \frac{1 \times 4}{4} = 2$. The rule is exactly obeyed (as it must be if there is only one type of oxygen). In more complicated cases with different oxygen sites or with oxygen and e.g., fluorine sites together in one structure, some deviations do occur although, again, in minerals the deviations are usually quite small, $n \pm 0.15$ where $n = 1, 2$. Developments of the theory are numerous, e.g., Ref. 16b, and theory still remains important as a guideline to the crystallographic site locations of, say, O, OH and F in a mineral, e.g., apatite, topaz or grunerite.^{16b} For synthetic materials, the deviations from PSCR are often greater, e.g., $n \pm 0.25$, and as will be noted later, the deviations are often in structures with important physical properties, i.e., ferro-electrics, fast ion conductors, etc.



PSCR does not apply to cations, but by incorporating bond length/bond strength considerations (that is, not considering all bonds at a cation to be of equal strength) and using a term of the Born repulsion type, Brown, Shannon and Wu (BSW)¹⁷⁻¹⁹ derive a bond sum of the type:

$$v \approx S = \sum_{i=1}^n K \left(\frac{R}{R_0} \right)^m$$

the K , R_0 and m constants for each cation around oxygen is empirically derived by computer refinement so that, in known common structures, the value of S is as near to v as possible. In this case, the bond sums at both cations and anions are fitted to nearly equal the valences. From this analysis emerges that the degree of covalence is unimportant, and that values of m concord with Born expectations (the Born concept is itself empirical). Furthermore, the concept introduced is that of force being the important bond consideration, rather than "where the electrons are thought to be", i.e., the force resulting from the electronic state is the more important factor rather than exactly how the force arises, whether by covalent or ionic bonding, etc. This is a viewpoint that is gaining currency. It is a useful simplification which may be inexplicable (Coulson is quoted as saying), but potentially enormously useful, belonging in the class of "convenient fictions" like "ionic radii".

What has not been done before is to use this type of analysis to attempt to predict isomorphous substituted types; given an oxide, i.e., a known mineral, can we predict that an isotypic mixed oxyfluoride, oxynitride, oxyfluoronitride might probably exist. This would be enormously valuable as we have a large range of mineral types that can be addressed. Moreover, more mineral types are discovered as having useful physical properties, e.g., ferroelectric fersnoite, so the prediction of related types could be valuable. Moreover, we should be able to predict the likely site occupancies of each anion, oxygen, fluorine and nitrogen.



PROBLEM

A series of mixed nitrogen containing crystal structures has recently been discovered; some have distinct new crystal types, e.g., LaSi_3N_5 ²⁰, $\text{Sc}_3\text{SiO}_5\text{N}$ ²¹ or BaSiN_2 ²² but many are isotypic with known, often mineral, forms. Thus, we have N-wollastonite, YSiO_2N ²³ N-mellilite,^{22,24} N-apatite,²⁶ N-wurtzite,^{24,28} N-cuspidine²⁵ and others.

With all the vast variety of minerals, could we have predicted these types from PSCR, and, if so, can yet undiscovered types be found? Could there be, e.g., a N-Fresnoite with unusual ferroelectric properties, or a N- β -alumina with exceptionally fast ion conductivity?

PROCEDURE

For relatively simple nitrides, say, $\text{Li}_2^{\text{IV}} \text{Zr}^{\text{VI}} \text{N}_2^{\text{VII}}$,²⁹ with one type of N, $S = 4 \times \frac{1}{4} + 3 \times \frac{4}{6} = 3$, or $\text{Th}^{\text{VIII}} \text{Be}^{\text{IV}} \text{N}_2^{\text{VI}}$,²⁹ one type of N, $S = 4 \times \frac{4}{8} + \frac{2 \times 2}{4} = 3$; these are trivial cases where S must equal 3. This is true of MnSiN_2 , Th_2SiN_4 , Ca_3N_2 , Be_3N_2 and so on.

With more than one type of N site, e.g., $\text{La}^{\text{VI}} \text{Si}_3^{\text{IV}} \text{N}_2^{\text{III}} \text{N}_3^{\text{IV}}$,²⁰ we find $S_{\text{N}(1)} = 3 \times \frac{4}{4} = 3$ and $S_{\text{N}(2)} = 2 \times \frac{3}{6} + 2 \times \frac{4}{4} = 3$, and again, exact agreement occurs. But this need not be so, although, to my knowledge, we have yet no example where the bond sums at N differ in a nitride.

For oxynitrides, more complexity is possible; in the simple case of $\text{Si}_2^{\text{IV}} \text{N}_2^{\text{III}} \text{O}^{\text{II}}$, $S_{\text{N}} = 3 \times \frac{4}{4} = 3$ and $S_{\text{O}} = 2 \times \frac{4}{4} = 2$, so that the N and O sites are strictly defined. For the wurtzite-like $\text{Li}^{\text{IV}} \text{Si}^{\text{IV}} \text{O}^{\text{IV}} \text{N}^{\text{IV}}$,²⁸ neutron diffraction indicates that N and O are ordered, N is linked to 3Si and 1Li, $S_{\text{N}} = 3 \times \frac{4}{4} + \frac{1}{4} = 3 \frac{1}{4}$, O is linked to 1Si + 3Li, $S_{\text{O}} = \frac{4}{4} + 3 \times \frac{1}{4} = 1 \frac{3}{4}$. This arrangement is one (probably the only one) leading to values near 2 (for O) and near 3 (for N) and might have been predicted. A range of $\pm 1/4$ is immediately suggested for consideration. This, perhaps encouraging case, is offset by cases such as Mg_2NF , rocksalt, all anion bond sums 2, and Al_2OC ,



all anion bond sums 3, which would not have been predicted. In the case of the AlON solid solutions, prototypically $\text{Al}_2\text{O}_3\cdot\text{AlN}$, the same applies, namely that all the anion sites have the same bond sum.

It is particularly instructive to look at a case where oxides, oxyfluorides and oxynitrides are already known in one crystal family, the cuspidines. Throughout we use numbering schemes and conventions from the cited references.

In Table 2 are the Brown, Shannon and Wu (BSW)¹⁷⁻¹⁹ bond sums for all ions and the PSCR sums for anions for cuspidine, $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$, which is a fairly rare mineral. The structure has been refined.³⁰ Each type of bond sum is automatically calculated by use of a computer program, DISTAG, originally written by Prof. Shiono at the University of Pittsburgh and modified by the author for this work. The input is the x,y,z parameters of each atom, the space group equivalent site symmetry generators, and the unit cell parameters. The program which normally calculates bond lengths and angles now searches the bond lengths to any maximum and calculates the respective sums given the BSW values for K, R_0 and m. For a complex structure, as here, this would be tedious and time-consuming by the hand method.

This structure is of low monoclinic symmetry, and all sites are non-equivalent. Perhaps we are not surprised that such a rare mineral does not closely obey PSCR. In sites assumed occupied by oxygen for the refinement O(1)-O(7), wide variations occur with a greatly overbonded site O(1) at 2.54 where the coordination is to 2Si and 2Ca. At the low bonded O(7) site, the sum is 1.82. We can expect a variation, then, of almost 0.45 to be allowed here for PSCR. For the BSW bond sums, the situation is only slightly better in that the O(1) site is now 2.22, but the lowest O site is 1.81 for O(2).

We are encouraged that BSW sums will be a better guide. Unfortunately, bond lengths, only obtainable from crystal refinements, are necessary in advance for the calculations. We will need the bond length/bond strength values for M-N and M-F bonds to proceed further and these have not yet been calculated, but should soon be available. When we assume the same values for



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Table 2
CUSPIDINE, $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2^*$

	BSW	PAULING
Si(1)	4.06	—
Si(2)	4.03	—
Ca(1)	2.09	—
Ca(2)	2.13	—
Ca(3)	1.90	—
Ca(4)	1.90	—
O(1)	2.22	2.54
O(2)	1.81	1.87
O(3)	1.77	1.90
O(4)	1.94	1.87
O(5)	1.90	1.91
O(6)	1.95	1.87
O(7)	1.91	1.82
F(1)	1.28	1.16
F(2)	1.32	1.07

*S. SABURI, ET AL. MIN. J. JAPAN 8 286 (1977)



M-F as for M-O, we see the F(1) and F(2) values in the table. The simple PSCR values are probably better at 1.16 and 1.07. They closely approximate 1 as expected and obey a rule, not perhaps too well-known, that F is never bonded to Si in silicate minerals.

The next step is to vary the valencies of the cations as for a substitution of Al^{3+} for Si^{4+} or Y^{3+} for Ca^{2+} , using the normal ionic radii and crystallochemical guidelines for likely substitutions; the program calculates the PSCR bond sums shown in Table 3. BSW sums for anions are calculated here for the isotypic $Eu_4Al_2O_9$ (the numbering of sites in the refinements of the latter and for $Ca_4Si_2O_7F_2$ is different in the literature). In general, comparing BSW and PSCR we see a better fit for the former. In terms of predictability of structures, had we started with cuspidine and attempted to predict the existence of $Y_4Al_2O_9$, we would have noted the low values at the 3 and 9 sites, but a better fit at the 5 site than cuspidine itself. For predicting $Y_4Si_2O_7N_2$, a known cuspidine,^{25,31} we would observe a low value at site 9, a high value at site 5 (2.86), very suitable for N and for other sites at 2.36 where another N might go. It is not possible scientifically to assert in advance, even the likelihood of the existence of the oxide or oxynitride cases here.

We must conclude immediately that poor Pauling bond sums do not rule out the existence of the isotypic species and may even suggest them. The question then remains as to the extent to which good bond sums actually imply the existence of a substituted isotype.

As a simple example, we may also consider mellilites (Table 4). For simplicity, we may consider these as tetrahedral sheet structures with 0 bridges within the sheets and 0 terminals at the edges of sheets bonding across to large cations between the sheets.^{32,33} For normal oxygen mellilites, Pauling bond sums are very variable (the very ability for a structure to have wide values probably accounts for the wide variety of substitutes that it may contain). The nitrogen substituted variety, in fact, more closely approximates good values with the conclusion that N is in the sheet bridging sites (with one left over) and the oxygen primarily in the terminal sites.



Table 3

CUSPIDINE - YTTRIUM ALUMINATE TYPES SPACE GROUP P2₁/c

ANION† POSITION	BSW	PAULING		
		Eu ₄ Al ₂ O ₉ †	Ca ₄ Si ₂ O ₇ F ₂	Y ₄ Al ₂ O ₉ Y ₄ Si ₂ O ₇ N ₂
1	2.04		1.91	2.11 2.36*
2	2.04		1.90	2.11 2.36*
3	1.73		1.82	1.68 1.93
4	1.88		1.87	2.11 2.36*
5	2.15		2.54	2.36 2.86*
6	1.92		1.87	2.04 2.29
7	1.73		1.87	2.11 2.36*
8	1.92		1.16*	1.79 1.79
9	2.16		1.07*	1.71 1.71

*IN CUSPIDINE, F GOES TO 8 AND 9, EACH FOUR COORDINATE TO CA ONLY.

†In Y₄Si₂O₇N₂, N GOES TO 5, FOUR COORDINATE TO 2Si AND 2Y, AND TO 1, 2, 4, OR 7, FOUR COORDINATE TO 1Si AND 3Y

†BRANDLE, C.D. AND STEINFINK, H., THE CRYSTAL STRUCTURE OF Eu₄Al₂O₉. INORG. CHEM. 8 1320-24, (1969).



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Table 4

MELLILITES

	ANION	BOND SUM
$\text{NaCaAlSi}_2\text{O}_7$		
$\text{Ca}_2\text{Al}_2\text{SiO}_7$		
$\text{Ca}_2\text{MgSi}_2\text{O}_7$		
$\text{Y}_2\text{Be}_2\text{SiO}_7$		
$\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$		
	O(ter)	1.5 - 2.125
	O(br)	1.75 - 2.25
	(ter)	2.125 2 SITES
	(br)	2.75 5 SITES



The last two cases suggest a guideline whereby N is most usually bonded to silicon in silicate oxynitrides (as opposed to F). Given the stability of the oxygen mellilites in spite of the poor Pauling bond sums, we would have predicted the possibility of the N-containing isotypes.

The α -wollastonites (Table 5) represents a case worthy of a close look. In order to explain the 'busy' table, in the first column for α - CaSiO_3 we have: Ca^{VIII} coordinated by 8 oxygens, Si^{IV} coordinated by 4 oxygens. Oxygens and silicons are in six membered alternating rings of Si and O. Oxygens coming off silicon in the ring are terminal, coordinating to 3Ca and Si for a bond sum of 1.75. Oxygens in the rings (bridging) are coordinated to 2Ca and 2Si for a bond sum of 2.50, which is extremely overbonded, accounting perhaps for the fact that α - CaSiO_3 is not the most stable form of wollastonite. For YSiO_2N , 23 O (term) is 2.13 and N (br) is 2.75 (note we assume that the terminal site contains O and the bridging site N because of these values). This fits the formula requirements exactly as there are twice the number of terminal positions as bridging ones. The closer approach of these bond sums to the 'ideal' values may explain why the α -wollastonite structure appears to be more stable, if not the only, form of YSiO_2N . As an aside, the availability of BSW calculations allows us to decide that YbBO_3 is probably an α -wollastonite too, for as in column 4, this type gives much better BSW bond sums than the former suggested type in column 5 (see Ref. 23 for details).

The apatites form an extremely flexible group of structures, and we begin to note that it is the structures with odd coordinations and long bonds which often facilitate this, and may also lead to special physical effects (as with the ferroelectric behavior of SbSI). In hydroxyapatite, there are two distinct Ca sites, each of which have "long bonds" which different authors have treated differently in their thinking of the bonding relationships. Here, we treat both cases and the BSW sums allow some judgement in this matter. Table 6 summarizes the situation where we include the long $\text{Ca}_\text{I}-\text{O}_{\text{III}}$ bonds in the coordination scheme. This leads to $\text{Ca}_\text{I}^{\text{IX}}$ and $\text{Ca}_{\text{II}}^{\text{VII}}$. For this scheme, the BSW sums come close to the valency values, suggesting that the "long bonds" are, indeed, contributing in $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and show the value of the BSW system. Pauling sums are also satisfactory for this case.



Table 5

COORDINATION AND BOND SUMS IN α - WOLLASTONITES

	α -CaSiO ₃	YSiO ₂ N	YbO ₃	
LARGE CATION	Ca ^{VIII} 80	Y ^{VIII} 6O + 2N	Yb ^{VIII} 80	Yb ^{VI} +Yb ^{XII} 6O 12O 2.82 2.03
				*
SMALL CATION	Si ^{IV} 40	Si ^{IV} 2O + 2N	B ^{IV} 40	B ^{IV} 40 2.91
ANION(S)	O ^{IV(ter)} 3Ca+Si 1.75	O ^{IV(ter)} 3Y+Si 2.13	O ^{IV(ter)} 3Yb+B 1.88	O ^{IV(ter)} 2Yb ^{VI} +Yb ^{XII} +B 1.95 1.81
	O ^{IV(br)} 2Ca+2Si 2.50	N ^{IV(br)} 2Y+2Si 2.75	O ^{IV(br)} 2Y+2B 2.50	O ^{IV(br)} 2Yb ^{XII} + 2B 2.35 1.85
PAULING ANION BOND SUMS			BSW BOND SUMS	

* EARLIER "PSEUDOVATERITE" STRUCTURE PROPOSED BY BRADLEY,
et al. SEE W.F. BRADLEY, D.L. GRAF, AND R.S. ROTH' ACTA CRYST. 20,
283 (1966).

Table 6

APATITE STRUCTURES **BOND SUM INCLUDING LONG BONDS OF** **Ca_I - O_{III} AND Ca_{II} - O_I TYPE**

POSITION	# ATOMS IN UNIT CELL	COORDINATION	BSW Ca ₅ (PO ₄) ₃ OH	APPROXIMATE BOND STRENGTH SUMS AT EQUIVALENT ANION SITES**		
Ca _I	4	9(3O _I +3O _{II} +3O _{III})	2.001			
Ca _{II}	6	7(OH+O _I +O _{II} +4O _{III})	2.057	Ca ₅ (PO ₄) ₃ F	"Y ₅ (SiO ₄) ₃ N"	Y ₅ (SiO ₃ N) ₃ □
P	6	4(O _I +O _{II} +2O _{III})	5.197			
O _I	6	4(P+2Ca _I +Ca _{II})	1.985	1.98	2.10	2.16
O _{II}	6	4(P+2Ca _I +Ca _{II})	2.077	1.98	2.10	2.16
O _{III}	12	4(P+Ca _I +2Ca _{II})	2.096	2.04	2.19	2.33 ≠
OH	2	3(Ca _{II})	1.000*	0.86	1.29	0

**USING PAULING'S SECOND CRYSTAL RULE, Sum = $\sum \frac{V}{cn}$; v = VALENCE, cn = COORDINATION #

*ASSUMED-CONFIRMED BY BOND SUM AT Ca_{II} NEARLY EQUAL TO 2.0.

≠ O_{III} SITES HALF FILLED WITH N.



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On this basis, then, when we look at $Y_5(SiO_4)_3N$, the formula originally proposed, we find no good site for N, although for a defect case, assuming a vacancy as a zero valent atom,³⁴ we improve the bond sum at the O_{III} site. As Y is a little smaller than Ca, and more formally highly charged, it could be expected that the coordination at Y might decrease so that it is effectively six coordinated by minor shifts of atoms causing the "long bonds" to become noncontributing. This is illustrated in Table 7. Now, the BSW values for $Ca_5(PO_4)_3OH$ become unsatisfactory, especially at Ca_I . The Pauling sums for $Ca_5(PO_4)_3OH$ also less well agree. But, we see a much better suggested site for N in " $Y_5(SiO_4)_3N$ ", and for the defect case, the O_{II} position appears to be where N would reside. Moreover, there are 3 O_{II} sites per formula unit, and if N goes here, then a nitrogen richer composition is possible than if N were restricted to 6 trigonal type OH site.

This analysis strongly supports the notion that N is bonded to Si in N-apatites, and that the formula is more closely represented by $Y_5(SiO_3N)_3$ than by " $Y_5(SiO_4)_3N$ "; nitrogen-rich apatites are indeed observed.²⁶ It is further suggested that Y^{3+} is coordinate in this compound.

$CaAl_4O_7$ ³⁵ is an interesting crystal structure where a nitrogen containing isotype is definitely predicted. Table 8 shows the coordination arrangement in this structure, with four independent anion sites, and the result of cation substitutions. The first column for $CaAl_4O_7$ shows the bond range for the structural type which is a variable type. The computer program, by substituting aliovalent ions in the Ca, Al(1) and Al(2) sites and calculating bond sums of the O(1)-O(4) sites, found 16 cases where each bond sum was $n \pm 0.30$ where $n = 1(F)$, $2(O)$, or $3(N)$ and where the restriction that the total bond sum at anions also equals the total valency of the cations.

Table 7

ALTERNATE APATITE SCHEME **ASSUMING LONG $\text{Ca}_I - \text{O}_{III}$ AND $\text{Ca}_{II} - \text{O}_I$ TYPE BONDS** **ARE NON-BONDING**

POSITION	#ATOMS IN UNIT CELL	COORDINATION	BSW ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$)	APPROXIMATE BOND STRENGTH SUMS AT EQUIVALENT ANION SITES**		
Ca_I	4	$6(3\text{O}_I + 3\text{O}_{II})$	1.622	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	" $\text{Y}_5(\text{SiO}_4)_3\text{N}$ "	$\text{Y}_5(\text{SiO}_3\text{N})_3\Box$
Ca_{II}	6	$6(\text{OH} + \text{O}_{II} + 4\text{O}_{III})$	1.907			
P	6	$4(\text{O}_I + \text{O}_{II} + 2\text{O}_{III})$	5.197			
O_I	6	$3(\text{P} + 2\text{Ca}_I)$	1.834	1.92	2.00	2.00
O_{II}	6	$4(\text{P} + 2\text{Ca}_I + \text{Ca}_{II})$	2.077	2.25	2.50	2.60 \neq
O_{III}	12	$3(\text{P} + 2\text{Ca}_{II})$	1.970	1.92	2.00	2.20
OH	2	(3Ca_{II})	1.000*	1.0	1.50	0

**USING PAULING'S SECOND CRYSTAL RULE, $\text{Sum} = \sum \frac{V}{cn}$; v = VALENCE, cn = COORDINATION#

* ASSUMED-CONFIRMED BY BOND SUM AT Ca_{II} NEARLY EQUAL TO 2.0

$\neq \text{O}_{II}$ SITES COMPLETELY FILLED WITH N.



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Table 8
Ca(Sr)Al₄O₇

Position	Coordination	Pauling Bond Sums		
		CaAl ₄ O ₇	"CaAl ₂ Si ₂ O ₅ N ₂ "	"CaP ₂ Al ₂ O ₃ N ₄ "
Ca ^{VIII}	O(1) + 4O(2) + 2O(3)			
Al(1) ^{IV}	2O(2) + O(3) + O(4)			
Al(2) ^{IV}	O(1) + O(3) + 2O(4)			
O(1) ^{III}	Ca + 2Al(2)	1.786	2.286	1.786
O(2) ^{IV}	2Ca + 2Al(1)	2.071	2.071	3.071 (N)
O(3) ^{III}	Ca + Al(1) + Al(2)	1.786	2.036	2.286
O(4) ^{III}	Al(1) + 2Al(2)	2.250	2.750 (N)	2.750 (N)

The second column illustrates the case for substitution of Al(2) by Si(2) so that the O(4) site, which has a bond sum of 2.750, becomes a potential site for N, while the other sites remain oxygen sites. For this reason, the synthesis of this compound was attempted. CaP₂Al₂O₃N₄ is the result of placing P in the Al(1) sites. We initially considered that compounds of that type were unlikely, but recently the compound LiPN₂ has been synthesized with P-N tetrahedra,⁴⁴ so if, indeed, mixed nitrogen phosphates can be produced, a huge array of mineral-like structures will become available.

The synthesis of "CaAl₂Si₂O₅N₂" proved to be difficult. Several techniques were tried including firing chemically prepared hydroxide mixtures in ammonia to ~ 1200°C, heating to higher temperatures to form glasses and then cooling, firing mixed Si₃N₄, CaCO₃ and Al(OH)₃, etc. in N₂/6% H₂ etc. About ten attempts were made in all, always with the result that mixtures were achieved which seemed to contain lines for "CaAl₂Si₂O₅N₂", but which also contained glasses and, in some cases, a N-gehlenite definitely was present.



This presumably has the formula: $\text{Ca}_2\text{AlSi}_2\text{O}_6\text{N}$, or possibly, if more N can enter, $\text{Ca}_2\text{Si}_3\text{O}_5\text{N}_2$. If the powders from these attempts were heated in air, $\text{CaAl}_2\text{Si}_2\text{O}_8$, Anorthite was formed.

Table 9 illustrates a similar analysis for the K_2NiF_4 group of structures³⁶ where N-containing species have been found.³⁷ For the oxyfluorides, which are well-known, it appears that F goes to the O(1) or apical site in octahedral sheets of small cations. However, for the nitrides, the N would occupy preferentially the bridging sites between the tetrahedra (Fig. 3). The structures with nitrogen in them do not obey PSCR well and could not have been predicted to exist by the approach here. Given the existence of K_2NiF_4 , the possibility of La_2NiO_4 e.g. is suggested; it is known.

Table 10 covers the $\beta\text{-K}_2\text{SO}_4$ types,³⁹ again, where N members have been found.⁴⁰ Using the parent K_2SO_4 data with the aliovalent substitutions, the KBaPO_4 and Ba_2SiO_4 types are predicted (they are known), but $\text{K}_2\text{PO}_3\text{F}$, which is known, would not be predicted. For $\text{LnEuSiO}_3\text{N}$ values calculated, again would not have allowed a prediction that the type might be stable. We see, again, that in the cases where prediction is not possible, it is for the phases which, in any case, do not always well obey Pauling's rule, even for the oxide case. We might be able to predict for structures that obey the rule as far as is known. Alternately, where the rule is not well obeyed is exactly where one might look for substitutional types regardless. However, even when the rule is not well obeyed, it is possible, to indicate the likely preferred sites for each anion species. For the K_2NiF_4 structures then, the lower valent anions will prefer the apical sites and the higher valent anions, the bridging sites.

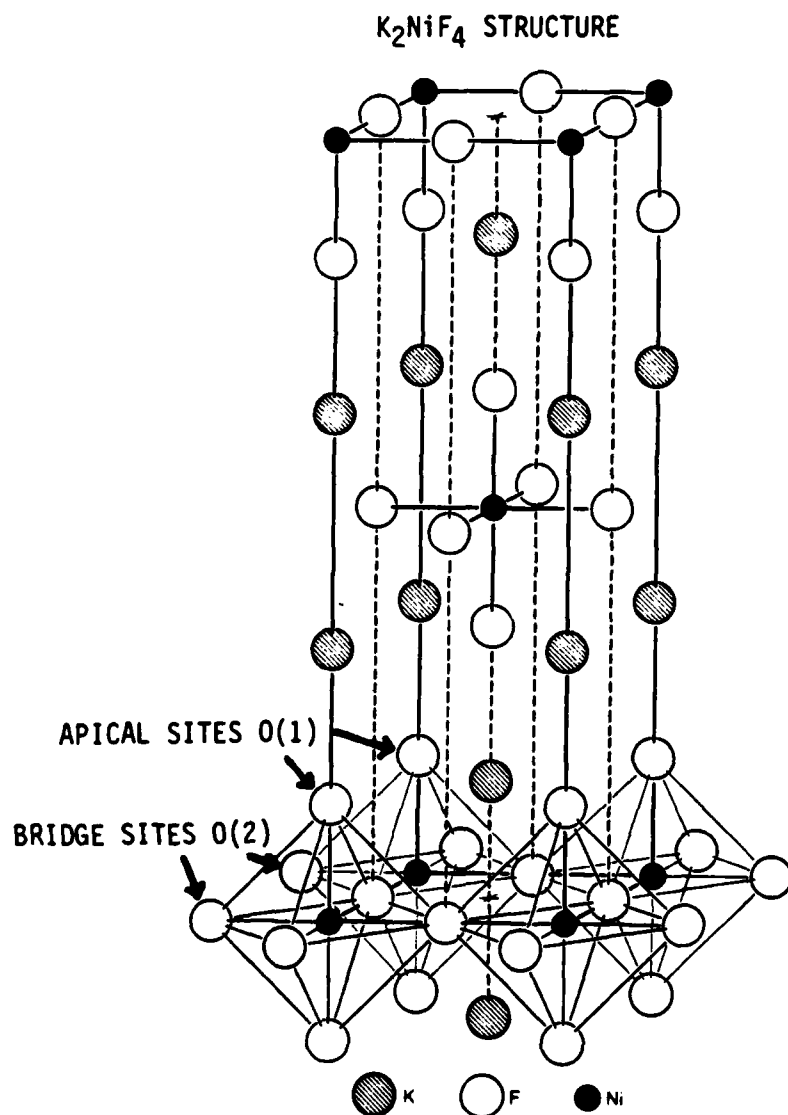


Fig. 3 The structure of K_2NiF_4 type showing the two anion sites.



Table 9
K₂NiF₄ Types

Position	Coordination	K ₂ NiF ₄	K ₂ TiO ₂ F ₂	Sr ₂ FeO ₃ F	Sr ₂ TiO ₄	La ₂ NiO ₄	LaSrAlO ₄	La ₂ AlO ₃ N	La ₂ TiO ₂ N ₂
Sr IX	50(1) + 40(2)								
Fe VI	20(1) + 40(2)								
O(1) VI Apical	5Sr + Fe	0.89	1.22	1.61	1.78	2.00	1.89	2.17	2.42
O(2) VI Bridge	4Sr + 2Fe	1.11	1.78	1.89	2.22	2.00	2.11	2.33	2.67

*NaLaTiO₄ is a most unusual type; Blasse reference in miscellaneous references.



Table 10
 β -K₂SO₄ Type

Position	Coordination	K ₂ SO ₄	K ₂ PO ₃ F	KBaPO ₄	Ba ₂ SiO ₄	LnEuSiO ₃ N ⁴⁰
K(1) ^{XI}	20(1) + 30(2) + 60(3)					
K(2) ^{IX}	30(1) + 20(2) + 40(3)					
S ^{IV}	0(1) + 0(2) + 20(3)					
O(1) ^{VI}	2K(1) + 3K(2) + S	2.015	1.65	1.947	2.030	2.364
O(2) ^{VI}	3K(1) + 2K(2) + S	1.995	1.94	2.018	1.990	2.030
O(3) ^{VI}	3K(1) + 2K(2) + S	1.995	1.94	2.018	1.990	2.030

More briefly, of the other structures analyzed, which are of interest to us, the magnetoplumbites and the whole family of β -alumina types show anomalously low bonded anion sites and do not well obey PSCR, although agreement with BSW estimates are better (Table 11). It is perhaps noteworthy that the LaMgAl₁₁O₁₉ structures more closely obey PSCR than the normal BaFe₁₂O₁₉ MP type. So also does CaMg₂Ti₂Al₈O₁₉ which is found as hibonite in meteorites.⁴² LaAl₁₂O₁₈N or BaMg₆Ti₆O₁₉ are not predicted within $n \pm 0.25$ and the former is not found, but the latter is known.⁴³ So, again, in this rather irregular structure type, little is gained by using PSCR, and it is noteworthy that large deviations from BSW values also occur.

In searching the literature, among the compounds found that obviously had an unknown structure was BaSiN₂,⁴⁵ the XRD powder pattern looked incomplete, and we considered it possible, too, that it might be an oxynitride in view of the stated sensitivity to water.



Table 11
BaFe₁₂O₁₉⁴¹

Position	Coordination	BSW	PSCR		
			BaFe ₁₂ O ₁₉	LaMgAl ₁₁ O ₁₉	CaMg ₂ Ti ₂ Al ₈ O ₁₉
Ba ^{XIII}	6 O(3) + 6 O(5)	2.288			
Fe(1) ^{VI}	6 O(4)	3.400			
Fe(2) ^V	2 O(1) + 3 O(3)	2.691			
Fe(3) ^{IV}	O(2) + 3 O(4)	2.632			
Fe(4) ^{VI}	3 O(3) + 3 O(5)	3.001			
Fe(5) ^{VI}	O(1) + O(2) +				
	2 O(4) + 2 O(5)	2.960			
O(1) ^{IV}	Fe(2) + 3 Fe(5)	1.862	2.100	2.10	1.90
O(2) ^{IV}	Fe(3) + 3 Fe(5)	1.920	2.250	2.25	2.25
O(3) ^V	2 Ba + Fe(2) +				
	2 Fe(4)	1.949	1.933	2.10	2.07
O(4) ^{IV}	Fe(1) + 2 Fe(3) +				
	2 Fe(5)	1.965	2.250	2.08	2.08
O(5) ^{IV}	Ba + Fe(4) +				
	2 Fe(5)	2.033	1.667	1.75	1.83

The material was made by firing Ba₃N₂ and Si₃N₄ powders together in N₂/6% H₂ to 1500°C in the correct ratio for BaSiN₂. The compound was formed nearly pure and it was immediately apparent that it was extremely water-sensitive, and was thereafter handled entirely in dry boxes. The x-ray diffraction pattern was run with the sample within a thin polyethylene bag containing phosphorous pentoxide; in this the sample was stable for a few hours. Table 12 gives the observed lattice spacings and intensities. Using the first 20 "d" values, the computer programs* deduced that the symmetry was

*We have evolved, over a three year period, programs suitable for small computers, using trial and error indexing, that are becoming quite powerful.



Table 12

BaSiN₂

Orthorhombic		B-Face Centered	
a = 0.5590 nm		i.e., $h + 1 = 2n$	
b = 0.7542 nm			
c = 1.1340 nm			
Possible space groups (36) or (63)			
d _{OBS}	d _{CALC}	I/I ₀	hkl
5.673	5.670	10	002
4.536	4.532	10	012
4.167	4.175	20	111
3.774	3.771	25	020
3.135	3.131	20	103
3.014	3.014	60	121
2.889	2.892	100	113
2.836	2.835	25	004
2.793	2.795	40	200
2.658	2.654	25	014
2.517	2.514	1	030*
2.500	2.507	1	202
2.3787	2.3790	15	212
2.2981	2.2982	40	032
2.2475	2.2455	28	220
2.1025	2.1016	2	105
2.0877	2.0877	5	222
2.0243	2.0245	15	115
1.9918	1.9904	7	204
1.9259	1.9245	10	214
1.8883	1.8900	25	006
	1.8855		040
1.8389	1.8387	10	301
1.7738	1.7752	30	232
1.6896	1.6896	10	026
1.6518	1.6527	10	321
1.6316	1.6317	15	313
1.5626	1.5631	23	240
1.5332	1.5330	1	216
1.5266	1.5280	10	323
1.5062	1.5069	1	242
1.4443	1.4445	3	151
1.3963	1.3975	7	400
+ many weak lines			

*This line is doubtful.



face centered orthorhombic with the lattice matrices, $a = 0.559$ nm, $b = 0.7542$ nm, $c = 1.1340$ nm, based on a higher angle refinement with B centering.

The chance that this is the correct unit cell is extremely high because of the centering and the presence of the key (002), (020) and (200) lines. The absence of (010) and (101) suggest the space groups (36) or (63).

Sensitivity to water is usually indicative of higher coordination for nitrogen. It is almost certain that the coordination scheme is $\text{Ba}^{\text{VIII}} \text{Si}^{\text{IV}} \text{N}_2^{\text{VI}}$. Nitrogen would be bonded by 4 bonds from Ba and 2 from Si so that the Pauling bond sum is $4 \times \frac{2}{8} + 2 \times \frac{4}{4} = 3$. The structure appears to be a new type as no isomorph in the Powder Diffraction File has been detected. Structures such as ThBeN_2 and BaZnO_2 ⁴⁶ were considered here. The XRD pattern is clearly similar to, but much more complete, than the one previously published⁴⁵ and we feel that the compound is, indeed, BaSiN_2 in formulation.

There is great interest in M^{3+} ions as sintering additives to Si_3N_4 , and the phase diagrams are most important in determining high temperature creep and oxidation properties. Sc^{3+} was considered because $\text{Sc}_2\text{Si}_2\text{O}_7$, thortveitite, is so stable in nature.

It seemed possible that there were no quaternary Sc-Si-O-N compounds. This was partly based on the similarity of the Sc^{3+} ionic radius (0.885Å) with those of Mg^{2+} and Zr^{4+} , both 0.86Å and both of which do not form such quaternary compounds, and the fact that no good candidates were predicted from the isomorphous/PSCR notions.

In earlier work, we did indeed make up several compositions which led to the finding that apparently at 1600°C-1800°C, $\text{Sc}_2\text{Si}_2\text{O}_7$, Sc_2O_3 and Si_3N_4 , and Si_3N_4 , $\text{Si}_2\text{N}_2\text{O}$ and $\text{Sc}_2\text{Si}_2\text{O}_7$ are phase compatible.⁴⁷ Curiously, we did not find Sc_2SiO_5 . As we were concerned with the Si_3N_4 -rich corner of the diagram for structural silicon nitride ceramic work, we did not investigate the scandia-rich corner where Thompson has found a compound he believes to be approximately $\text{Sc}_3\text{SiO}_5\text{N}$, denoted 'Q' phase.²¹ We thought to briefly investigate it for possible isomorphous types. Using Thompson's formula, we obtained mixtures of 'Q', Sc_2O_3 and $\beta\text{-Si}_3\text{N}_4$ when firing appropriate quantities of



$\text{Sc}_2\text{O}_3\text{-Si}_3\text{N}_4$ in N_2 to 1700°C . The XRD powder pattern of the first 20 lines is shown in Table 13. It is obviously the same phase as Thompson's, and even though we have many more lines, the computer indexing failed to find a convincing unit cell of monoclinic symmetry or higher. We believe the structure could be triclinic. Attempts to prepare 'Q' starting with $\text{Si}_2\text{N}_2\text{O}$ instead of Si_3N_4 produced an apparently similar, but not identical, phase. We feel there may be a set of polytypic phases here, as in the AlN-rich corner of the Si-Al-O-N diagram, so that the existing patterns of 'Q' could also be mixtures of these or other metastable configurations. As a result of these investigations, it was possible to achieve a new formulation of Si_3N_4 with superior creep resistance.⁴⁶

Table 13
Q-Phase, " $\text{Sc}_3\text{SiO}_5\text{N}$ "

d_{OBS}	I/I_0	d_{OBS}	I/I_0
7.675	5	2.2796	2
5.206	2	2.2204	4
3.382	7	2.1585	10
2.923	80	2.0813	6
2.8747	100	1.8831	18
2.8284	90	1.7783	19
2.6873	35	1.7036	10
2.5177	20	1.6656	20
2.4467	25	1.6305	5
2.3494	10	1.5819	5

In view of the possible nonequilibrium conditions, we feel that the compound may be in the region of the phase diagram not earlier investigated by us, and that the configuration may be more nitrogen-rich than Thompson's estimate.



The magnetoplumbites are now a very well-known group of compounds because of a variety of uses: magnetic, fluorescent, radwaste incorporators, and so on. As mentioned earlier, bond sums did not suggest a good N candidate (but then, the MP's themselves do not obey the PSCR well) and none was found. Because the $\text{LaAl}_{11}\text{O}_{18}$ type is only formed and stable at high temperature (the temperature increasing as the ionic radius of the rare earth diminishes), it would be easy to spot if a compound of the type $\text{LaAl}_{12}\text{O}_{18}\text{N}$ were formed. This compound would be the case of a coupled substitution of La^{3+} for a divalent such as Ba^{2+} with balance by N^{3-} replacing O^{2-} .

Several chemical techniques were tried: gel type mixtures of Dispural[®] type $\text{AlO}(\text{OH})$ and either La or Y nitrates were fired in ammonia to 1500°C , or gel type mixtures with added AlN were fired in NH_3 or $\text{N}_2/6\% \text{H}_2$ to 1500°C – 1700°C .

In the La case, the formation of a MP related phase was kinetically stimulated, but a careful analysis of lattice parameters revealed the MP type phase to have the identical values to $\text{LaAl}_{11}\text{O}_{18}$ and, moreover, always Al_2O_3 or AlN was left in excess, suggesting that the 1:12 composition could not be reached. We conclude that, in some way, nitrogen (or hydrogen) may speed the kinetics, but not be significantly a part of the product. In the case of Yttrium, where no $\text{YAl}_{11}\text{O}_{18}$ phase is known, no formation of a MP related type occurred which would have been a parallel to hibonite $\text{CaAl}_{12}\text{O}_{19}$ (i.e., $\text{YAl}_{12}\text{O}_{18}\text{N}$).

A large number of structures have been briefly reviewed for possible N-containing isotypes: wadeites, fresnoites, danburite/hurlbutite, herderites, agrellite, RR^* type, and a group of oxyfluoride minerals. The feature which emerges is that there may well be a very large number of N-phosphate compounds that are isotypic with silicates. Time constraints have prevented any attempts to synthesize these cases, but they should be speedily attempted. We expect, e.g., CaPO_2N to exist and probably be a wollastonite.



CONCLUSION

1. When the PSCR rule applies well in an oxide, as in most minerals, then we can expect that for stable N-substituted isotypes the rule will still apply well. This is the case for some simple nitrides, e.g., Mg_3N_2 (antibixbyite), Th_2SiN_4 (Ca_2SiO_4 type), AlN or MgSiN_2 (wurtzite), etc. If calculations indicate that poor agreement would be achieved in N-substitution, i.e., sums not within ± 0.25 of whole numbers, then it appears unlikely that the compound would form. A compound of type 2 below being preferred on a new type or none at all.
2. When PSCR rule applies poorly in an oxide, as for apatite, cuspidine and generally rarer mineral types, and also for many synthetic materials with odd properties such as β -aluminas, then nitrogen substituted cases obey the rule often even more poorly. But it is just in these cases where N-substitution is sometimes encountered (other factors, radii, electropositivity, etc., permitting). So the place to look is where, because of the poor agreement, the likelihood cannot be strictly predicted.
3. In spite of the proviso in 2 above, in many cases (but not always), the position of the nitrogens in the anion lattice can be predicted. In many instances, certain anion sites have clearly higher values than others, and here is where the nitrogens should be located. For the only case studied by neutron diffraction, LiSiON , this is so. As for this case, it is expected that the nitrogen will tend to be bonded to the higher valent cations in mixed structures. In the cases studied containing Si, the nitrogen seems to be preferentially bonded to this higher valent element. For the same reason, nitrogen will generally be in a different site in oxynitrides



than fluorine in oxyfluorides. This is clearcut for the apatite cases.

4. There is an indication that a whole family of nitrogen phosphate compounds may exist, especially with P-N rings, substituting for Si-N rings, as for wollastonites and wadeites etc.



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